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18JUL03 E823627-1 D02481
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1. Your reference	P34671-/NBR/MEA	
2. Patent application number *(The Patent Office will fill in this part)*	0316863.0	18 JUL 2003
3. Full name, address and postcode of the or of each applicant *(underline all surnames)*	Hamilton Erskine Limited 17 Moss Road, Ballygowan Newtownards, Co Down BT23 6JQ, Northern Ireland	
Patents ADP number *(if you know it)*		8676413001
If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom	
4. Title of the invention	"Improvements Relating to Glass"	
5. Name of your agent *(if you have one)*	Murgitroyd & Company	
"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Scotland House 165-169 Scotland Street Glasgow G5 8PL	
Patents ADP number *(if you know it)*	1198015	

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day / month / year)*
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))*	Yes	

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Continuation sheets of this form	-
Description	15
Claim(s)	-
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Drawing(s)	6 +6 Jel

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Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	-
Request for preliminary examination and search *(Patents Form 9/77)*	-
Request for substantive examination *(Patents Form 10/77)*	-
Any other documents *(please specify)*	-

11. I/We request the grant of a patent on the basis of this application.

Signature Murgitroyd & Company
Murgitroyd & Company

Date
17 July 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

Mark Earnshaw 0141 307 8400

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Notes

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Improvements Relating to Glass

The present invention relates to improved ballistic and blast- and hurricane-resistant optically transparent composite materials involving glass.

There have been many suggestions for "bullet-proof" and "blast-proof" transparent windows and the like, either for civilian purposes such as for use in aircraft, or for military purposes, especially protection against enemy and terrorist attack. However, with the developing threat from international terrorism and events such as those of September 11 2001, many governments and major organisations are re-appraising their security requirements. High velocity weapons and better explosives are increasingly available to terrorists and the like. Whilst traditional 'bullet-proof' glass will still be required, there is now an increasing need for certain key installations, persons and equipment, especially in and around military and high governmental locations, to be

protected against a higher level of threat than previously considered necessary.

Where pure optical transmission for a window is not a necessity, there are many available materials having high strength and impact resistance. However, where optical transparency of 'normal' windows and glazing is desired, e.g. for military base houses and offices, current forms of glazing are only adequate for protection against low velocity bullets (e.g. from small arms), and low levels of blast. Most current forms of 'bullet proof' glass use several layers of glass bonded by adhesive polymer film. The energy of the projectile is dissipated over increasingly large areas of blast. To some extent the projectile can be deformed or fragmented and can be deviated from the original line of attack. The energy is directed towards a direction different to the previous path, resulting in further dissipation of energy, e.g. as shown in figure 1.

Typical design solutions involve either glass/glass combinations or glass/polycarbonate (PC) combination. The latter offer an advantage in that they are lighter than the former, but they often have delamination problems. The effect of bonding of PC to glass is also difficult as PC has a substantially higher rate of thermal expansion than glass. This causes high stress levels in the bonding interlayer during temperature changes which often leads to delamination.

The PC designs are often 'complex', particular as the level of protection required increases. The number of layers can cause problems with optical interference and secondary image formation because of the number of glass/PC interfaces. There may also be weight or thickness limitations preventing their use in particular applications. This is shown in the following tables.

Weapon type & Calibre	Class	Design	Thickness (mm)	Weight (kg/m^2)	Transmittance (%)
Hand Gun 9mm Luger	BR2/C1	6^{2}PC5^{2}3-12-ESG6	35	47	77
Rifle 0.223 (5.56*45)hc	BR5/C3	8^{2}6^{2}PC6^{2}6^{2}PC6	39	71	64
		8^{2}PC8^{2}6-12-6^{2}PC8^{2}3-20-ESG6	82	95	?
Rifle 0.308 (7.62*51)	BR6/C4	8^{2}8^{2}6^{2}PC6^{2}6^{2}PC6	49	93	?
		8^{2}PC8^{2}3-12-10^{2}PC8^{2}3-20-ESG6	85	102	?
Rifle 0.308 (7.62*51)hc	BR7/C5	6^{2}8^{2}8^{2}PC8-20-6^{2}8^{2}82PC8	91	143	58

US5665450 discusses the introduction of glass fibres and glass ribbons into transparent composites, but, as it states, the introduction of glass fibres into

an optically transparent polymer destroys the transparency of the polymer.

US5665450 considers that the introduction of glass ribbons provide a higher degree of optical clarity and lower level of distortion than glass fibres. However the photographs in US5665450 indicating the degree of optical clarity of fibre and ribbon-reinforced materials still show distortion even based on photographic reproduction of relatively indistinctive photographs. Figure 7 shows percentage like transmission as a function of temperature and wavelength. However, it can be seen that the percentage transmission barely gets above 80% at the lowest temperature and highest wavelength measured. The lowest temperature measured is at 30°C, which is also not a temperature generally encountered in many countries on a regular basis. It is interesting that the percentage transmission in US5665450 was not measured at more temperate or freezing temperatures. Moreover, 80% optical transmission is very poor in comparison with the expectancy of 'normal' glass, which should be at least 90% at all temperatures. It is appreciated that the human eye can easily recognise or perceive a less than 100% optical transmission of light through a 'transparent' material.

In essence, there is a requirement for an optically transparent composite material having about or at least 90% optical transmission over a range of temperatures, including below 0°C, and also able to

withstand high velocity ballistic projection whilst having a relatively low manufacturing cost.

According to one aspect of the present invention, there is provided an optically transparent composite material comprising at least one glass/resin/glass lamination, wherein the resin is a PRR material having optical fibre-reinforcement therein.

The term "PRR" refers to 'polycarbonate replacement resins', a range of materials provided by Chemetall GmbH of Frankfurt, Germany, and generally defined in their International Patent Application No WO 01/38087A1. The PRR materials are a range of transparent cast resins that can consist of reactive acrylate and methacrylate monomers, acrylate and methacrylate oligomers, bonding agents and initiators. The content of WO 01/38087A1 defining these materials is incorporated herein by way of reference.

The term "PRR" also extends to similarly provided polyurethane resins, often termed "PUR".

A range of commonly available PRR materials are sold under the trade name Naftlolan®. The Naftlolan materials are provided in a range of different formulations to provide slightly different properties. A list of product data of certain polyurethene Naftlolan materials are listed in Tables 2 and 3 hereinafter, by way of example only.

PRR materials have been found to have several advantages over previously used polymer glass lamination layers. Firstly, the refractive index of PRR material overlaps very closely with many types of glass. Secondly, PRR materials have been found to expand and contract at very close rates with that of glass, thus leading to minimal if ever cracking or delamination (due to internal stress) during any thermal expansion and contraction of the composite material. Thirdly, PRR materials are relatively very easy to use and set in transparent composite materials, especially compared with processes of curing previously used types of polymers and resins. They are also useable in designs incorporating complex curves.

Because PRR materials have a co-efficient of expansion and contraction very close to glass, these materials are usable to provide optically transparent composite materials with glass over a much greater range of temperatures than, e.g. that shown in US5665450. In particular, the present invention is designed to provide a ballistic-resistant optically transparent composite material which is usable at temperatures even as low as -15°C to -40 °C, generally -20°C, e.g. the temperature of windows in military installations in certain countries such as Canada, as well as temperatures going up to 30°C to 40°C, such as the temperature of windows in more tropical countries. To that extent, the difference in co-efficiency of glass, such as a

normal silica-based glass, and PRR materials, deviates little over a wide temperature range.

Table 4 hereinafter lists the refractive indices of a number of resins, including a number of the Naftolan range, indicating their close refractive index to that of glass in general.

In general, the refractive index of the PRR materials are sufficiently close to readily available types of glass, such as a silica-based glass, that the optical transparency of the composite material of the present invention is as good as that from any current glass/glass or glass/PC laminations.

The fibre reinforcement in the PRR layer of the composite material of the present invention can be provided by any know type of "fibre material", being for instance in the form of filaments, or in the form of particles such as beads, or even powders, as long as such fibre material wholly or very substantially has the same refractive index as glass across all or most the wavelengths of optical light. Such glass fibres are well known in the art, one such available product being sold under the trade name Tyglas by Fothergill Engineered Fabrics.

The fibre reinforcement provide the PRR intermediate layer with improved strength because of their well known ability to laterally transmit impact energy. Meanwhile, PRR materials also have improved utility

as a resin to band the fibre material fillers because of their similar co-efficient of thermal expansion and adhesive strength to glass.

In the present invention, the thickness of the glass and PRR layers, and the density of fibre reinforcement in the PRR layer, can vary according to the qualities of the final composite material desired. Cost and physical properties are factors in considering the thickness of the layers. One known ratio of thickness is glass/PRR/glass of 6/20/4mm; this is provided by way of example only.

Indeed, a major facet of PRR material is that its strength is independent of its thickness. Many types of resins and adhesives only have strength for a minimal thickness, as their use is to bond together the layers (e.g. of glass) on each side, rather than provide any inherent strength of their own right. PRR has been found not only to provide good bonding to glass, but also have internal strength in its own right. The thickness of the PRR layer is therefore independent of the thickness of the glass layers either side.

The nature of "high velocity ballistic protection" can be defined in general terms as the difference between a hand gun and a rifle, e.g. above a NATO 5.56 or 7.62mm ball.

According to a second aspect of the present invention, there is provided a process for making an

optically transparent composite material as herein before defined, comprising the steps admixing the PRR material with the optical fibre-reinforcement, and allowing the combination to cure and set between the two layers of glass.

Further information on the curing of PRR resins may be found in WO 01/38087A1.

Meanwhile, increasing power and sophistication of explosive-technology, means that 'blast-proof' optically transparent material is also desired having increasing strength. In this regard, it is now generally desired to provide blast-resistant optically transparent material having the ability to withstand a blast of 500kg TNT or equivalent at 40m.

US patent No 3953630 discloses a laminated transparent assembly suitable for use as a windscreen for a high speed vehicle wherein high strength flexible material is embedded in a plastic material, laid between two layers of glass. The flexible material extends beyond the transparent assembly, so as to be directly conjoined with the structure of the vehicle. Thus, as any blast causes deformation of the transparent assembly (as part of the impact absorption), the high strength flexible material provides a direct bond between the vehicle structure bolts and the transparent assembly, hopefully thereby resisting complete separation of the two and travel of the transparent assembly into the vehicle.

However, US3953630 only discloses the use of polyvinylbutyral (PVB) as the plastic layered to provide the bonding between the glass sheets and the flexible material. In addition, manufacture of the transparent assembly in US3953630 requires an altering of the conventional laminating technique, in order to provide good bonding between a number of PVB sheets, and the glass. This requires pre-heating treatment, insertion of the full assembly including glass sheets in a closed bag to evacuate all air, followed by heating in a autoclave with high pressure. This method of manufacture has not lent itself to cost-efficient production for a number of transparent assemblies, other than for the very special uses such as our aircraft windscreens as mentioned.

Moreover, PVB in particular is a material only designed to provide good bonding between glass layers. It is typically only 1-2mm thick. Further thickness of layer is not desired, as PVB has little internal strength in its own right.

In a third aspect of the present invention, there is provided a laminated optically transparent assembly comprising at least one glass/resin/glass lamination, and having one or more high tensile strength flexible material reinforcement pieces extending laterally from the resin layer to provide increased attachment of the assembly to a surround, wherein the resin is a PRR material.

PRR materials are those as defined herein above. As well as the greater similarity of refractive index and co-efficient of thermal expansion of PRR material to glass, the PRR-flexible material and PRR-glass bonding has been found to be superior to that of prior materials such as PVB.

Meanwhile, the assembly of the present invention still provides the degree of flexibility desired for a blast-resistant window, with the reinforced attachment of the window to the surround, such as the window rebate of frame.

The high tensile strength flexible material may be similar to that disclosed in US3953630, i.e. woven fabric or woven glass fibre material or polyester fibre material. One such product is Kevlar®.

Preferably, the flexible material extends wholly or substantially around opposites sides of the complete transparent assembly, to provide flexibility of attachment to the surround.

As for the ballistic-resistant material described hereinabove, the thickness of the glass and resin layers of the blast-resistant assembly can follow those well known in the art. One suitable dimension for the glass/resin/glass in 4m glass, 4mm PRR and 3mm glass.

The thickness of the PRR layer can indeed be up to 40-50mm thick, as PRR has inherent strength independent of thickness as mentioned above. To that extent, the PRR material can be as thick and therefore as strong as desired, as all the strength from a blast is taken by the resin (whilst any glass shatters).

The ability to provide a PRR layer of any thickness provides a further benefit.

Thus, according to a forth aspect of the present invention, there is provided a blast-resistant composite material comprising at least one layer of PRR material having at least one reinforcement piece extending wholly or substantially across the PRR layer.

Preferably, the reinforcement piece is a series of strips of bars or other reinforcement means, more preferably forming a grid or grid-like structure wholly or substantially across the composite material.

The PRR material is that as defined hereinabove. The reinforcement piece can be one or more of woven rovin, webbing, webbing material or even metal material. The use of a metallic grid provides the same effect as a "muntin" system which uses metallic reinforcement grid alongside a glazing panel, but not actually therein. The present invention therefore achieves the same effect and strength as a

muntin system, but as a one piece assembly, thereby significantly reducing assembly and installation.

The blast-resistance is achieved because the PRR layer can be any thickness desired, e.g. up to 40-50mm, which is able to accommodate reinforcement pieces, whereas previous resins were not able to achieve such thickness, and thereby accommodate reinforcement therein.

The benefit of achieving reinforcement within the PRR material is that each 'section' created by the reinforcement piece or pieces, e.g. each small section within the grid, can be regarded as having its own frame, as thus regarded as a separate section in terms of analysis against blast. As is well known in the art, the blast-resistance of a small section is greater than that of a large section. By dividing the composite panel into a number of small sections, significant blast-resistance is achieved.

It is noted that the optical transparency of blast-resistant panels using the muntin system is not as important as that described for other aspects of the present invention, so that the comparative refractive index is not as important as that as described above in relation to other aspects of the present invention.

It will be recognised by these skilled in the art the composite materials and assemblies could also be

used to provide hurricane or the like resistance, and thus the present invention is extended thereto. Embodiments of the present invention will now be described by way of example only and with reference to the accompanying drawings in which:

Figure 1 is schematic cross-sectional view of the impact of a projectile against a current multi-glass laminated window pane;

Figure 2 is a cross-sectional view of a optically transparent composite material according to one embodiment of the present invention;

Figure 3 is a laminated optically transparent assembly according to a second embodiment of the present invention.

As previously mentioned, figure 1 shows how the energy of a projectile is dissipated over increasingly large areas of glass of a known glass PC lamination pane, leading to a large area of glass shattered from the left hand side.

Figure 2 shows a optically transparent composite material 2 comprising a glass/resin/glass lamination. Within the PRR resin layer 4 are a series of traditional fibre glass woven rovings 6.

To produce the material, the rovings 6 were secured between two panes of glass 8, and the PRR resin 4 was injected into the cavity. The resin 4 flows up

the inside of the glass 8 and disperses through the woven roving 6, wetting the fibres and forming an excellent bond.

Figure 3 shows a blast-resistant assembly 10 mounted to a wall 12. Between the two panes of glass 14, a 2 inch wide unidirectional glass fibre woven roving 16 was bonded into the same PRR resin 18 as mentioned above. The complete assembly 10 was located in the rebate of a window frame 20, and the roving reinforcement material 16 fixed to the frame 20 by adhesive, and also by means of a lateral bolt 22.

The assembly 10 was tested in a Hannsfield 20k-w tensometer. Loads in access of 8000N were applied before the fibre woven 16 broke. Considerably greater loads could be achieved with the use of thicker fibres or different types of fibres.

The present invention provides ballistic-resistant and blast-resistant assemblies providing protection against much higher levels of protection from high velocity weapons and explosives than currently known with current forms of glazing. Production of the assemblies is also comparatively simple and cost effective compared to previous types of similar assemblies, which used less suitable polymers and plastic material.

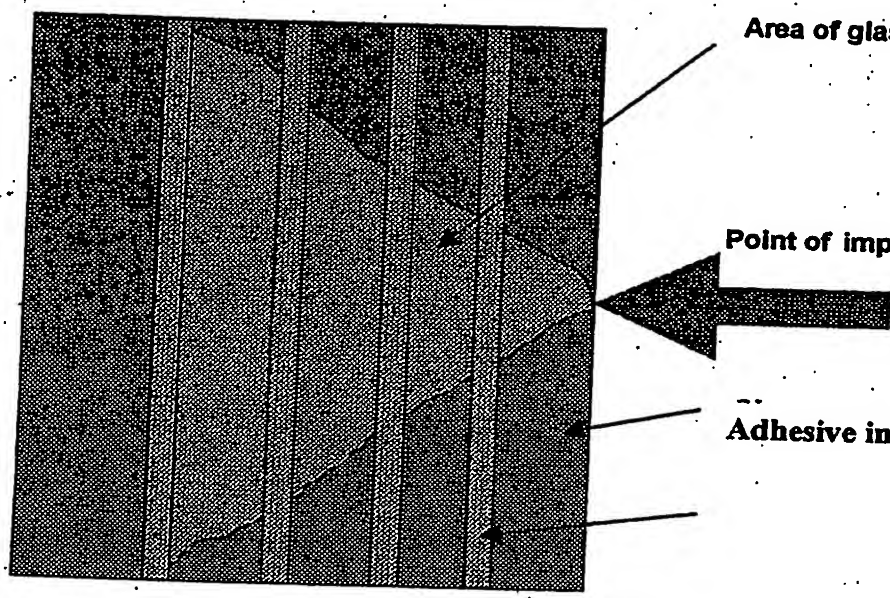
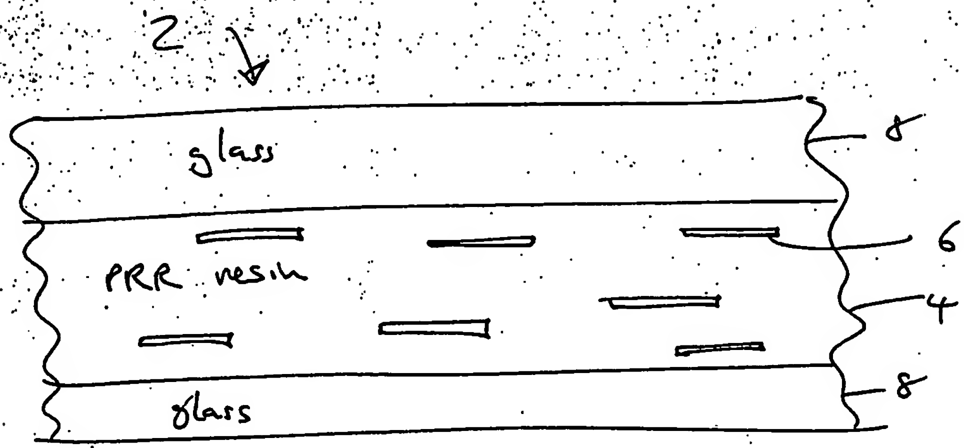
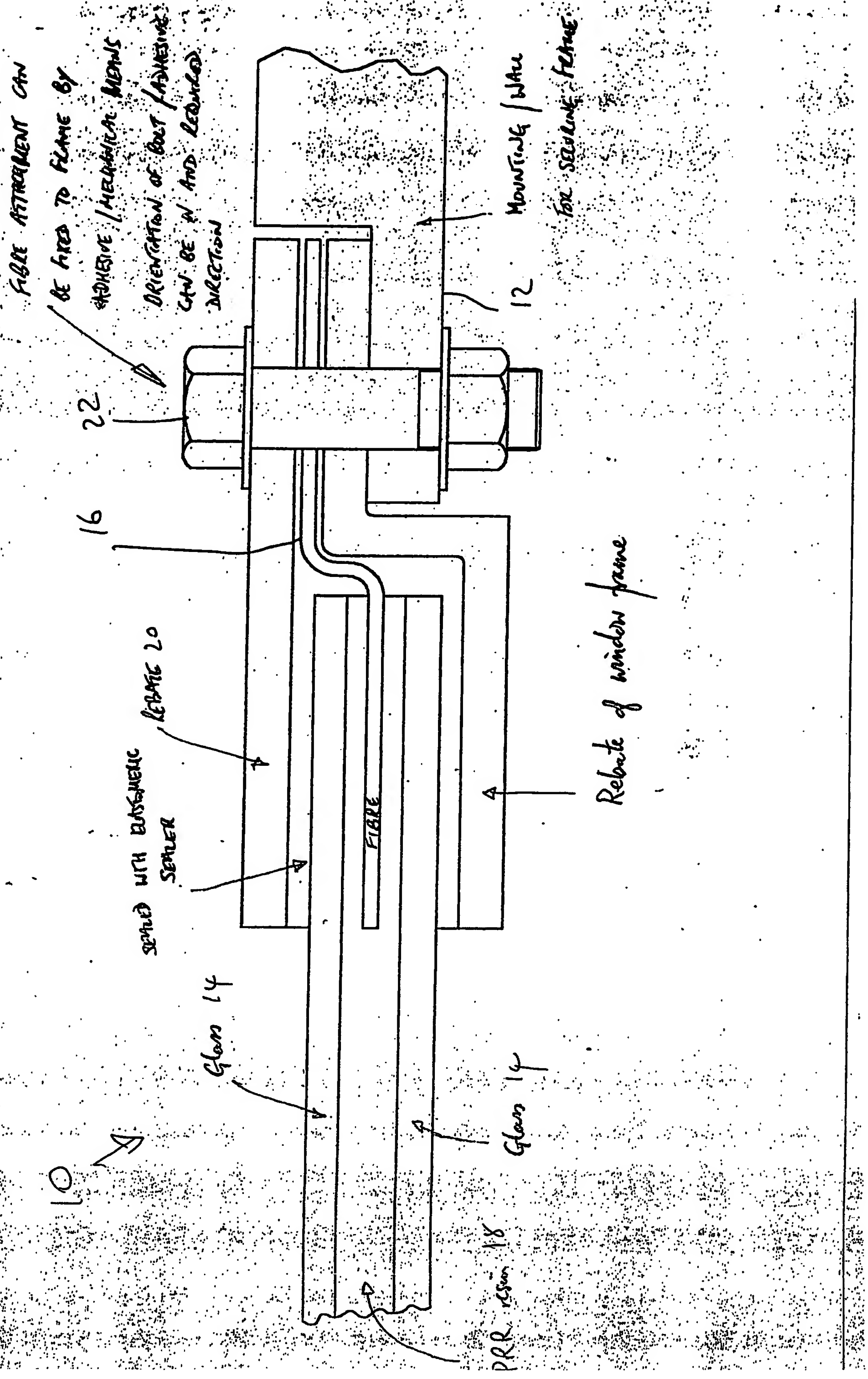

Area of glass destroyed by impact
Point of impact
Adhesive interlayer

Fig 1

2/6

Fig 2




FIBRE ATTACHMENT CAN BE FIXED TO FRAME BY ADHESIVE / MECHANICAL MEANS ORIENTATION OF BOLT / ADHESIVE CAN BE IN AND REQUIRED DIRECTION
MOUNTING / WALL FOR SECURING FRAME
12
22
16
REBATE 20
SEALED WITH ELASTOMERIC SEALER
FIBRE
Rebate of window frame
Glass 14
Glass 14
10
PRR resin 18
F-3 3

4/6

Product Data of Polyurethan Composite Materials

Physical Properties	Naftolan PU-A 700 / PU-B 304	Naftolan PU-A 206 / PU-B 606	Naftolan VP-PA 0911 / VP-PB 2110	Naftolan VP-PA 1011 / VP-PB 2110	Naftolan VP-PA 2601 / VP-PB 2110	Naftolan VP-PA 0511 / VP-PB 2910	Standard
Density							
Max							
Min							
Range possible in one layer							
Strength & Stiffness							
Tensile strength [Mpa]	16	16	19	18	5	2.1	DIN 53 504
25% module [Mpa]	5	1.2	15	6	1.2	0.7	DIN 53 504
50% module [Mpa]	6	1.7	14	7	1.8	1.2	DIN 53 504
100% module [Mpa]	8	2.5	15.5	10	3.2	1.9	DIN 53 504
Tensile modulus							
Tensile yield point							
Elongation at break [%]	180	360	150	160	150	120	DIN 53 504
Compressive strength							
Compressive modulus							
Compressive yield point							
Flexural strength							
Flexural modulus (also called modulus of elasticity)							DIN EN ISO 527
Flexural yield point							
In-plane shear strength							
In-plane shear modulus							
Toughness							
Variation with loading rate							
Hardness							
Shore A hardness	90	73	85	80	65	55	DIN 53 505
Adhesion to glass							
Bond shear strength							
Compression shear strength [Mpa] 4/2/4 mm glass/ glass	18	7.5	20	20	10	2.5	
Thermal							
Thermal coefficient of expansion							
Thermal conductivity							
Specific heat capacity (at 20 oC)							
Resistance							
Resistivity							
Temperature coefficient of resistance							

These values are for guidance only and do not represent a specification.

Product Data of Polyurethan Composite Materials

5/6

Physical Properties		Naftolan PU-A 700 / PU-B 304	Naftolan PU-A 206 / PU-B 606	Naftolan VP-PA 0911 / VP-PB 2110	Naftolan VP-PA 1011 / VP-PB 2110	Naftolan VP-PA 2601 / VP-PB 2110	Naftolan VP-PA 0511 / VP-PB 2910	Standard
Flammability								
Melting point								
Boiling point		Because of the moleculare structure, the materials do not melt and boil						
Smoke emission		Because of the moleculare structure, the materials do not melt and boil						
Critical Oxygen Index (COI) (minimum oxygen fraction in an oxygen-nitrogen mixture which will support steady state combustion of the plastic. Plastics with COI >0.21 are self extinguishing)								
Chemical Resistance								
Acids								
Alkalis		The materials are not resistant against Alkalis						
Organic solvents		The resistance against organic solvents depends very much on the tested solvents						
Weatherability/degradation								
Ageing – temp cycling test		Tests according to DIN 1286 with different kind of laminates were passed without failures.						
UV absorption		See the transmission datas on the next sheets						
Adsorption of water								
Additional Data								
Viscosity (23°C) [mPa's]	Component A	450	320	600	515	435	360	
Viscosity (23°C) [mPa's]	Component B	3250	85	85	85	85	85	
Viscosity (23°C) [mPa's]	Mixture	2550	200	225	200	245	230	
Specific weight (23°C) [g/cm³]	Component A liqu	1.02	1.01	1.03	1.02	1.02	1.01	
Specific weight (23°C) [g/cm³]	Component B liqu	1.04	1.05	1.05	1.05	1.05	1.05	
Specific weight (23°C) [g/cm³]	Mixture liquid	1.04	1.037	1.04	1.03	1.03	1.02	
Volume Shrinking [%]		2	2	4	4	3	2	
Processing time (23°C) [min]		45	15	40	30	30	30	
Curing time(23°C) [h]		12	48	12	24	24	12	
Storage time before delivery (18°C to 23 °C) [d]		4	6			4		
Shore A hardness after 1 day (cured resin) DIN		65		75	65	50	40	
Shore A hardness after 7 days (cured resin)		90	73	95	90	65	55	
thermal coductivity (DIN 52612) [W/(m*K)]		0.18						DIN 52612
transmittance (DIN 67507) (assembly 6/8/4mm) [%]		90						
transmittance (DIN 67507) (assembly 6/15/4mm) [%]		88						DIN 67 507
transmittance (DIN 67507) (assembly 6/20/4mm) [%]		88						DIN 67 507
								DIN 67 507

These values are for guidance only and do not represent a specification.

Table 4

Refractive Index
liquid / cured Resins (at 20°C)

Resin	n_{D20} liquid	n_{D20} cured
UV 11	1,4362	-
UV 22	1,4417	1,4813
UV 33	1,4396	-
ICE-Gießharz EP 1309-103	1,4434	-
UV 203	1,4370	1,4713
S 700 M	1,4299	-
S 696 M	1,4272	-
Naftolan VP-PA 0511	1,4542	-
Naftolan VP-PA 1011	1,4568	1,4844 *
Naftolan PU-A 206	1,4540	-
Naftolan VP-PB 2110	1,4169	-
Naftolan PU-B 606	1,4777	-
Naftolan VP-PA 2601	1,4553	-
Naftolan PU-A 700	-	-
Naftolan PU-B 304	1,4739	-

* cured with corresponding B component